RESTRICTED ROTATION IN ARYL OLEFINS

BY

MATTHEW WILLIAM MILLER

B.S., Montana State College, 1936

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS,
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RESTRICTED ROTATION IN ARYL OLEFINS

INTRODUCTION

In 1928 Adams and his students[1,2] suggested that aryl olefins with large groups in the *ortho*-positions and on the olefinic carbon atoms should possess restricted rotation about the aromatic-olefinic bond. If the aryl group was unsymmetrically substituted, these aryl olefins should exist in enantiomorphic forms capable of being separated by the usual methods of resolution.

Since *o*-(β,β-dimethyl-α-isopropylvinyl)-phenyltrimethylammonium iodide[3] was the only true aryl olefin which had been resolved, it was the purpose of this investigation to find suitable methods for the synthesis of this class of compounds, especially methods which would make feasible the preparation of several closely related olefins to allow a study of the effect of different groups around the point of restricted rotation.

DISCUSSION OF EXPERIMENTAL

β-Mesityl-β-chloroacrylic Acids

Restricted rotation in aryl olefins was demonstrated by resolving β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic acid and β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-acrylic acid. These acids were prepared by carbonating the enol-magnesium bromides of bromopropiomesitylene and bromoacetomesitylene,[4] and treating the β-ketonic acids thus obtained with phosphorus pentachloride and phosphorus oxychloride.[5]

The enantiomorphs of the α-methylacrylic acid were not racemized by refluxing for twelve hours in glacial acetic acid. The enantiomorphs of the acrylic acid were racemized when refluxed in *n*-butyl alcohol. The half-life period at the temperature of refluxing *n*-butyl alcohol was 178 minutes.

The necessity for unsymmetrical substitution in the benzene ring was proven by bromination and chlorosulfonation of the active forms of β-chloro-β-(2,4,6-trimethyl-3-bromophenyl)-α-methylacrylic acid. Bromination resulted in an inactive, symmetrical dibromo compound. Chlorosulfonation resulted in unsymmetrical, active 5-chlorosulfonyl derivatives.

Mesitylacetic Acids

In this series, α-chlorovinylmesitylene[6] was converted to 3-(α-chlorovinyl)-2,4,6-trimethylphenylacetic acid by chloromethylation, forming the nitrile, hydrolyzing the nitrile to the amide and diazotizing the amide. Attempts to resolve this acid by fractional crystallization of the quinine salt failed.

This synthesis was extended to α-chloropropenylmesitylene and α-chloroisobutenylmesitylene and carried as far as the formation of the nitriles, 3-(α-chloropropenyl)-2,4,6-trimethylbenzyl cyanide and 3-(α-chloroisobutenyl)-2,4,6-trimethylbenzyl cyanide.

β-(α-Naphthyl)-acrylic Acids

A third method of synthesis was attempted by preparing 9-methoxy-2-methyl-4,3-β-naphthopyrone.[7] This pyrone formed mono-nitro and mono-bromo derivatives in the 10 position but would not undergo addition reactions on the olefin bond in the pyrone ring. For this reason tetra-substituted olefins could not be prepared by opening the pyrone ring and methylating the 2-hydroxyl group.

The acrylic acids formed by opening the pyrone ring and methylating the 2-hydroxyl group had *trans*-configurations whereas those formed by condensing 2,7-dimethoxynaphthaldehyde with propionic anhydride and potassium propionate and then substituting had *cis*-configurations.

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VITA

The writer was born March 14, 1915, in Columbus, Montana. He attended the public schools in that vicinity and spent one year at Columbus High School. He then attended Gallatin County High School for three years. His undergraduate training was received at Montana State College, from which he received the degree of Bachelor of Science in 1936. The same year he entered the Graduate School of the University of Illinois. He was a teaching assistant at the University of Illinois during the years 1936-1939. He held the Eastman Kodak Fellowship during the year 1939-1940.